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Test Methods for Evaluating Solid Waste Physical/ Chemical Methods

Produced by the *U.S. Environmental Protection Agency, Office of Solid Waste* and the *U.S. Department of Commerce, National Technical Information Service*

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- It contains the entire, official version of the Third Edition manual with Final Updates I, II, IIA, and IIB already integrated, including all diagrams, figures, and flow charts.

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EPA plans to periodically revise this CD-ROM version to include all future final updates to the manual.

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CHAPTER NINE

SAMPLING PLAN

9.1 DESIGN AND DEVELOPMENT

The initial -- and perhaps most critical -- element in a program designed to evaluate the physical and chemical properties of a solid waste is the plan for sampling the waste. It is understandable that analytical studies, with their sophisticated instrumentation and high cost, are often perceived as the dominant element in a waste characterization program. Yet, despite that sophistication and high cost, analytical data generated by a scientifically defective sampling plan have limited utility, particularly in the case of regulatory proceedings.

This section of the manual addresses the development and implementation of a scientifically credible sampling plan for a solid waste and the documentation of the chain of custody for such a plan. The information presented in this section is relevant to the sampling of any solid waste, which has been defined by the EPA in its regulations for the identification and listing of hazardous wastes to include solid, semisolid, liquid, and contained gaseous materials. However, the physical and chemical diversity of those materials, as well as the dissimilarity of storage facilities (lagoons, open piles, tanks, drums, etc.) and sampling equipment associated with them, preclude a detailed consideration of any specific sampling plan. Consequently, because the burden of responsibility for developing a technically sound sampling plan rests with the waste producer, it is advisable that he/she seek competent advice before designing a plan. This is particularly true in the early developmental stages of a sampling plan, at which time at least a basic understanding of applied statistics is required. Applied statistics is the science of employing techniques that allow the uncertainty of inductive inferences (general conclusions based on partial knowledge) to be evaluated.

9.1.1 Development of Appropriate Sampling Plans

An appropriate sampling plan for a solid waste must be responsive to both regulatory and scientific objectives. Once those objectives have been clearly identified, a suitable sampling strategy, predicated upon fundamental statistical concepts, can be developed. The statistical terminology associated with those concepts is reviewed in Table 9-1; Student's "t" values for use in the statistics of Table 9-1 appear in Table 9-2.

9.1.1.1 Regulatory and Scientific Objectives

The EPA, in its hazardous waste management system, has required that certain solid wastes be analyzed for physical and chemical properties. It is mostly chemical properties that are of concern, and, in the case of a number of chemical contaminants, the EPA has promulgated levels (regulatory thresholds) that cannot be equaled or exceeded. The regulations pertaining to the management of hazardous wastes contain three references regarding the

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TABLE 9-1. BASIC STATISTICAL TERMINOLOGY APPLICABLE TO SAMPLING PLANS FOR SOLID WASTES

Terminology	Symbol	Mathematical Equation	(Equation)
• Variable (e.g., barium or endrin)	x	—	
• Individual measurement of variable	x_i	—	
• Mean of possible measurements of variable (population mean)	μ	$\mu = \dfrac{\sum\limits_{i=1}^{N} x_i}{N}$, with N = number of possible measurements	(1)
• Mean of measurements generated by sample (sample mean)	$\bar{x}$	Simple random sampling and systematic random sampling $\bar{x} = \dfrac{\sum\limits_{i=1}^{n} x_i}{n}$, with n = number of sample measurements	(2a)
		Stratified random sampling $\bar{x} = \sum\limits_{k=1}^{r} W_k\,\bar{x}_k$, with $\bar{x}_k$ = stratum mean and W_k = fraction of population represented by Stratum k (number of strata [k] range from 1 to r)	(2b)
• Variance of sample	s^2	Simple random sampling and systematic random sampling $s^2 = \dfrac{\sum\limits_{i=1}^{n} x_i^2 - (\sum\limits_{i=1}^{n} x_i)^2/n}{n-1}$	(3a)
		Stratified random sampling $s^x = \sum\limits_{k=1}^{r} W_k\,s_k^2$, with s^x_k = stratum variance and W_k = fraction of population represent by Stratum k (number of strata [k] ranges from 1 to r)	(3b)

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TABLE 9-1. (Continued)

Terminology	Symbol	Mathematical equation	(Equation)
• Standard deviation of sample	s	$s = \sqrt{s^2}$	(4)
• Standard error (also standard error of mean and standard deviation of mean) of sample	$s_{\bar{x}}$	$s_{\bar{x}} = \dfrac{s}{\sqrt{n}}$	(5)
• Confidence interval for μ[a]	CI	$CI = \bar{x} \pm t_{.20}\, s_{\bar{x}}$, with $t_{.20}$ obtained from Table 2 for appropriate degrees of freedom	(6)
• Regulatory threshold[a]	RT	Defined by EPA (e.g., 100 ppm for barium in elutriate of EP toxicity)	(7)
• Appropriate number of samples to collect from a solid waste (financial constraints not considered)	n	$n = \dfrac{t^2_{.20}\, s^2}{\Delta^2}$, with $\Delta = RT - \bar{x}$	(8)
• Degrees of freedom	df	$df = n - 1$	(9)
• Square root transformation	---	$X_i + 1/2$	(10)
• Arcsin transformation	---	Arcsin p; if necessary, refer to any text on basic statistics; measurements must be converted to percentages (p)	(11)

[a]The upper limit of the CI for μ is compared with the applicable regulatory threshold (RT) to determine if a solid waste contains the variable (chemical contaminant) of concern at a hazardous level. The contaminant of concern is not considered to be present in the waste at a hazardous level if the upper limit of the CI is less than the applicable RT. Otherwise, the opposite conclusion is reached.

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TABLE 9-2. TABULATED VALUES OF STUDENT'S "t" FOR EVALUATING SOLID WASTES

Degrees of freedom (n-1)[a]	Tabulated "t" value[b]
1	3.078
2	1.886
3	1.638
4	1.533
5	1.476
6	1.440
7	1.415
8	1.397
9	1.393
10	1.372
11	1.363
12	1.356
13	1.350
14	1.345
15	1.341
16	1.337
17	1.333
18	1.330
19	1.328
20	1.325
21	1.323
22	1.321
23	1.319
24	1.318
25	1.316
26	1.315
27	1.314
28	1.313
29	1.311
30	1.310
40	1.303
60	1.296
120	1.289
	1.282

[a]Degrees of freedom (df) are equal to the number of samples (n) collected from a solid waste less one.

[b]Tabulated "t" values are for a two-tailed confidence interval and a probability of 0.20 (the same values are applicable to a one-tailed confidence interval and a probability of 0.10).

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sampling of solid wastes for analytical properties. The first reference, which occurs throughout the regulations, requires that <u>representative</u> samples of waste be collected and defines representative samples as exhibiting average properties of the whole waste. The second reference, which pertains just to petitions to exclude wastes from being listed as hazardous wastes, specifies that enough samples (but in no case less than four samples) be collected over a period of time sufficient to represent the <u>variability</u> of the wastes. The third reference, which applies only to ground water monitoring systems, mandates that four replicates (subsamples) be taken from each ground water sample intended for chemical analysis and that the mean concentration and <u>variance</u> for each chemical constituent be calculated from those four subsamples and compared with background levels for ground water. Even the statistical test to be employed in that comparison is specified (Student's t-test).

The first of the above-described references addresses the issue of <u>sampling accuracy</u>, and the second and third references focus on <u>sampling variability</u> or, conversely, <u>sampling precision</u> (actually the third reference relates to analytical variability, which, in many statistical tests, is indistinguishable from true sampling variability). Sampling accuracy (the closeness of a sample value to its true value) and sampling precision (the closeness of repeated sample values) are also the issues of overriding importance in any scientific assessment of sampling practices. Thus, from both regulatory and scientific perspectives, the primary objectives of a sampling plan for a solid waste are twofold: namely, to collect samples that will allow measurements of the chemical properties of the waste that are both accurate and precise. If the chemical measurements are <u>sufficiently accurate and precise</u>, they will be considered <u>reliable</u> estimates of the chemical properties of the waste.

It is now apparent that a judgment must be made as to <u>the degree of sampling accuracy and precision</u> that is required to estimate reliably the chemical characteristics of a solid waste for the purpose of comparing those characteristics with applicable regulatory thresholds. Generally, high accuracy and high precision are required if one or more chemical contaminants of a solid waste are present at a concentration that is close to the applicable regulatory threshold. Alternatively, relatively low accuracy and low precision can be tolerated if the contaminants of concern occur at levels far below or far above their applicable thresholds. However, a word of caution is in order. Low sampling precision is often associated with considerable savings in analytical, as well as sampling, costs and is clearly recognizable even in the simplest of statistical tests. On the other hand, low sampling accuracy may not entail cost savings and is always obscured in statistical tests (i.e., it cannot be evaluated). Therefore, although it is desirable to design sampling plans for solid wastes to achieve only the minimally required precision (at least two samples of a material are required for any estimate of precision), it is prudent to design the plans to attain the greatest possible accuracy.

The roles that inaccurate and imprecise sampling can play in causing a solid waste to be inappropriately judged hazardous are illustrated in Figure 9-1. When evaluating Figure 9-1, several points are worthy of consideration. Although a sampling plan for a solid waste generates a mean concentration ($\overline{X}$) and standard deviation (s, a measure of the extent to which individual sample concentrations are dispersed around $\overline{X}$) for each chemical contaminant of concern, it is not the variation of individual sample concentrations that is of ultimate concern, but rather the variation that characterizes $\overline{X}$ itself. That measure of dispersion is termed the standard deviation of the mean (also, the standard error of the mean or standard error) and is designated as $s_{\overline{X}}$. Those two sample values, $\overline{X}$ and $s_{\overline{X}}$, are used to estimate the interval (range) within which the true mean (μ) of the chemical concentration probably occurs, under the assumption that the individual concentrations exhibit a normal (bell-shaped) distribution. For the purposes of evaluating solid wastes, the probability level (confidence interval) of 80% has been selected. That is, for each chemical contaminant of concern, a confidence interval (CI) is described within which μ occurs if the sample is representative, which is expected of about 80 out of 100 samples. The upper limit of the 80% CI is then compared with the appropriate regulatory threshold. If the upper limit is less than the threshold, the chemical contaminant is not considered to be present in the waste at a hazardous level; otherwise, the opposite conclusion is drawn. One last point merits explanation. Even if the upper limit of an estimated 80% CI is only slightly less than the regulatory threshold (the worst case of chemical contamination that would be judged acceptable), there is only a 10% (not 20%) chance that the threshold is equaled or exceeded. That is because values of a normally distributed contaminant that are outside the limits of an 80% CI are equally distributed between the left (lower) and right (upper) tails of the normal curve. Consequently, the CI employed to evaluate solid wastes is, for all practical purposes, a 90% interval.

9.1.1.2 Fundamental Statistical Concepts

The concepts of sampling accuracy and precision have already been introduced, along with some measurements of central tendency ($\overline{X}$) and dispersion (standard deviation [s] and $s_{\overline{X}}$) for concentrations of a chemical contaminant of a solid waste. The utility of $\overline{X}$ and $s_{\overline{X}}$ in estimating a confidence interval that probably contains the true mean (μ) concentration of a contaminant has also been described. However, it was noted that the validity of that estimate is predicated upon the assumption that individual concentrations of the contaminant exhibit a normal distribution.

Statistical techniques for obtaining accurate and precise samples are relatively simple and easy to implement. Sampling accuracy is usually achieved by some form of random sampling. In random sampling, every unit in the population (e.g., every location in a lagoon used to store a solid waste) has a theoretically equal chance of being sampled and measured. Consequently, statistics generated by the sample (e.g., $\overline{X}$ and, to a lesser degree, $s_{\overline{X}}$) are unbiased (accurate) estimators of true population parameters (e.g., the CI for μ). In other words, the sample is representative of the population. One of the commonest methods of selecting a random sample is to divide the

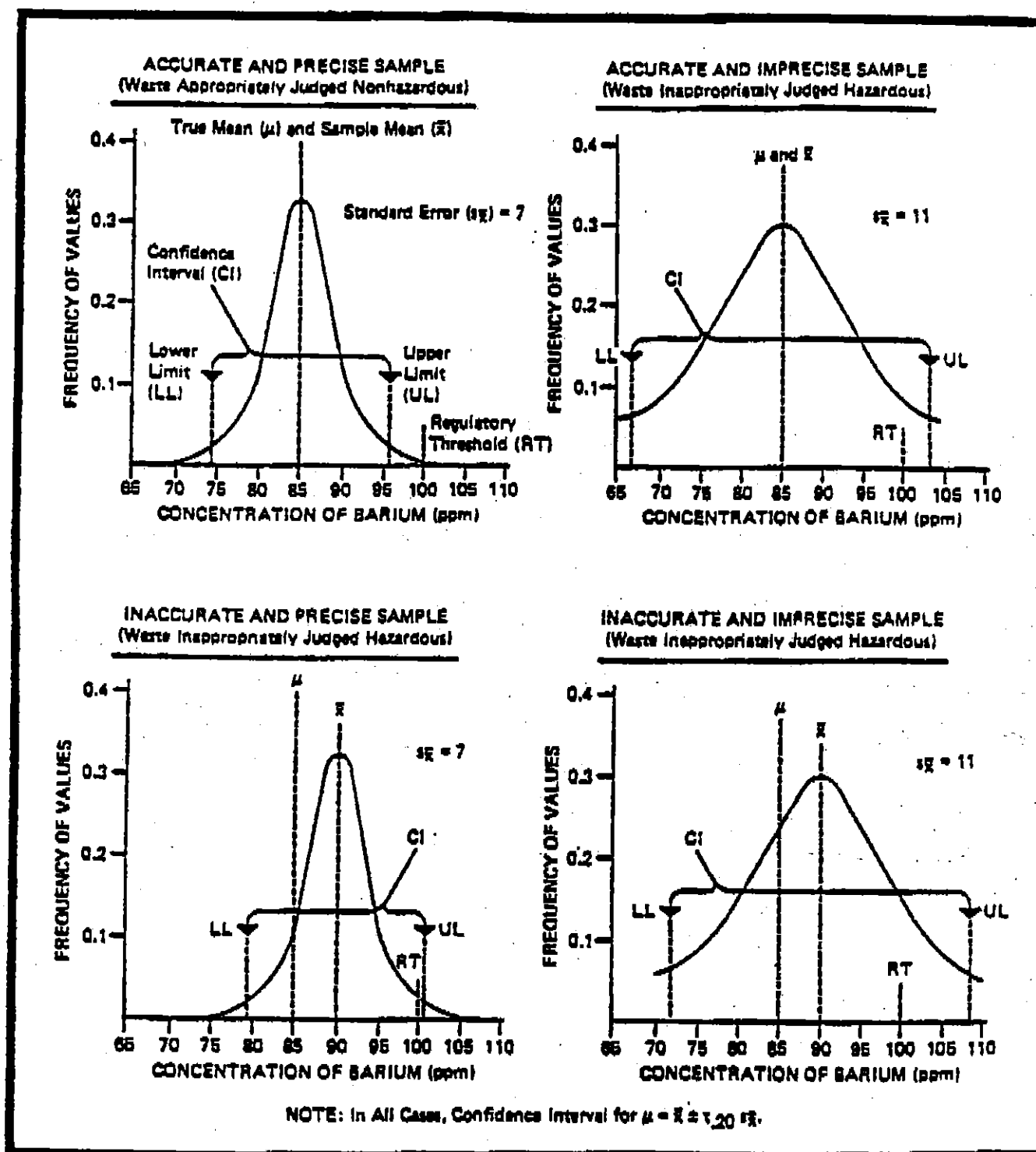Revision ___0___
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Figure 9-1.—Important theoretical relationships between sampling accuracy and precision and regulatory objectives for a chemical contaminant of a solid waste that occurs at a concentration marginally less than its regulatory threshold. In this example, barium is the chemical contaminant. The true mean concentration of barium in the elutriate of the EP toxicity test is 85 ppm, as compared to a regulatory threshold of 100 ppm. The upper limit of the confidence interval for the true mean concentration, which is estimated from the sample mean and standard error, must be less than the regulatory threshold if barium is judged to be present in the waste at a nonhazardous level.

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population by an imaginary grid, assign a series of consecutive numbers to the units of the grid, and select the numbers (units) to be sampled through the use of a random-numbers table (such a table can be found in any text on basic statistics). It is important to emphasize that a haphazardly selected sample is not a suitable substitute for a randomly selected sample. That is because there is no assurance that a person performing undisciplined sampling will not consciously or subconsciously favor the selection of certain units of the population, thus causing the sample to be unrepresentative of the population.

Sampling precision is most commonly achieved by taking an appropriate number of samples from the population. As can be observed from the equation for calculating $s_{\bar{x}}$, precision increases ($s_{\bar{x}}$ and the CI for μ decrease) as the number of samples (n) increases, although not in a 1:1 ratio. For example, a 100% increase in the number of samples from two to four causes the CI to decrease by approximately 62% (about 31% of that decrease is associated with the critical upper tail of the normal curve). However, another 100% increase in sampling effort from four to eight samples results in only an additional 39% decrease in the CI. Another technique for increasing sampling precision is to maximize the physical size (weight or volume) of the samples that are collected. That has the effect of minimizing between-sample variation and, consequently, decreasing $s_{\bar{x}}$. Increasing the number or size of samples taken from a population, in addition to increasing sampling precision, has the secondary effect of increasing sampling accuracy.

In summary, reliable information concerning the chemical properties of a solid waste is needed for the purpose of comparing those properties with applicable regulatory thresholds. If chemical information is to be considered reliable, it must be accurate and sufficiently precise. Accuracy is usually achieved by incorporating some form of randomness into the selection process for the samples that generate the chemical information. Sufficient precision is most often obtained by selecting an appropriate number of samples.

There are a few ramifications of the above-described concepts that merit elaboration. If, for example, as in the case of semiconductor etching solutions, each batch of a waste is completely homogeneous with regard to the chemical properties of concern and that chemical homogeneity is constant (uniform) over time (from batch to batch), a single sample collected from the waste at an arbitrary location and time would theoretically generate an accurate and precise estimate of the chemical properties. However, most wastes are heterogeneous in terms of their chemical properties. If a batch of waste is randomly heterogeneous with regard to its chemical characteristics and that random chemical heterogeneity remains constant from batch to batch, accuracy and appropriate precision can usually be achieved by simple random sampling. In that type of sampling, all units in the population (essentially all locations or points in all batches of waste from which a sample could be collected) are identified, and a suitable number of samples is randomly selected from the population. More complex stratified random sampling is appropriate if a batch of waste is known to be nonrandomly heterogeneous in terms of its chemical properties and/or nonrandom chemical heterogeneity is known to exist from batch to batch. In such cases, the population is stratified to isolate the known sources of nonrandom chemical heterogeneity.

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After stratification, which may occur over space (locations or points in a batch of waste) and/or time (each batch of waste), the units in each stratum are numerically identified, and a simple random sample is taken from each stratum. As previously intimated, both simple and stratified random sampling generate accurate estimates of the chemical properties of a solid waste. The advantage of stratified random sampling over simple random sampling is that, for a given number of samples and a given sample size, the former technique often results in a more precise estimate of chemical properties of a waste (a lower value of $s_{\bar{x}}$) than the latter technique. However, greater precision is likely to be realized only if a waste exhibits substantial nonrandom chemical heterogeneity and stratification efficiently "divides" the waste into strata that exhibit maximum between-strata variability and minimum within-strata variability. If that does not occur, stratified random sampling can produce results that are less precise than in the case of simple random sampling. Therefore, it is reasonable to select stratified random sampling over simple random sampling only if the distribution of chemical contaminants in a waste is sufficiently known to allow an intelligent identification of strata and at least two or three samples can be collected in each stratum. If a strategy employing stratified random sampling is selected, a decision must be made regarding the allocation of sampling effort among strata. When chemical variation within each stratum can be estimated with a great degree of detail, samples should be <u>optimally allocated</u> among strata, i.e., the number of samples collected from each stratum should be directly proportional to the chemical variation encountered in the stratum. When detailed information concerning chemical variability within strata is not available, samples should be <u>proportionally allocated</u> among strata, i.e., sampling effort in each stratum should be directly proportional to the size of the stratum.

Simple random sampling and stratified random sampling are types of <u>probability sampling</u>, which, because of a reliance upon mathematical and statistical theories, allows an evaluation of the effectiveness of sampling procedures. Another type of probability sampling is <u>systematic random sampling</u>, in which the first unit to be collected from a population is randomly selected, but all subsequent units are taken at fixed space or time intervals. An example of systematic random sampling is the sampling of a waste lagoon along a transect in which the first sampling point on the transect is 1 m from a randomly selected location on the shore and subsequent sampling points are located at 2-m intervals along the transect. The advantages of systematic random sampling over simple random sampling and stratified random sampling are the ease with which samples are identified and collected (the selection of the first sampling unit determines the remainder of the units) and, sometimes, an increase in precision. In certain cases, for example, systematic random sampling might be expected to be a little more precise than stratified random sampling with one unit per stratum because samples are distributed more evenly over the population. As will be demonstrated shortly, disadvantages of systematic random sampling are the poor accuracy and precision that can occur when unrecognized trends or cycles occur in the population. For those reasons, systematic random sampling is recommended only when a population is essentially random or contains at most a modest stratification. In such cases, systematic random sampling would be employed for the sake of convenience, with little expectation of an increase in precision over other random sampling techniques.

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ich an individual who is well acquainted with the solid waste to be sampled selects a sample without regard to randomization. The validity of data gathered in that manner is totally dependent on the knowledge of the sampler and, although valid data can sometimes be obtained, authoritative sampling is not recommended for the chemical characterization of most wastes.

It may now be useful to offer a generalization regarding the four sampling strategies that have been identified for solid wastes. If little or no information is available concerning the distribution of chemical contaminants of a waste, simple random sampling is the most appropriate sampling strategy. As more information is accumulated for the contaminants of concern, greater consideration can be given (in order of the additional information required) to stratified random sampling, systematic random sampling, and, perhaps, authoritative sampling.

The validity of a CI for the true mean (μ) concentration of a chemical contaminant of a solid waste is, as previously noted, based on the assumption that individual concentrations of the contaminant exhibit a <u>normal distribution</u>. This is true regardless of the strategy that is employed to sample the waste. Although there are computational procedures for evaluating the correctness of the assumption of normality, those procedures are meaningful only if a large number of samples are collected from a waste. Because sampling plans for most solid wastes entail just a few samples, one can do little more than superficially examine resulting data for obvious departures from normality (this can be done by simple graphical methods), keeping in mind that even if individual measurements of a chemical contaminant of a waste exhibit a considerably abnormal distribution, such abnormality is not likely to be the case for sample means, which are our primary concern. One can also compare the mean of the sample ($\overline{X}$) with the variance of the sample (s^2). In a normally distributed population, $\overline{X}$ would be expected to be greater than s^2 (assuming that the number of samples [n] is reasonably large). If that is not the case, the chemical contaminant of concern may be characterized by a <u>Poisson distribution</u> ($\overline{X}$ is approximately equal to s^2) or a <u>negative binomial distribution</u> ($\overline{X}$ is less than s^2). In the former circumstance, normality can often be achieved by transforming data according to the <u>square root transformation</u>. In the latter circumstance, normality may be realized through use of the <u>arcsine transformation</u>. If either transformation is required, all subsequent statistical evaluations must be performed on the transformed scale.

Finally, it is necessary to address the <u>appropriate number of samples</u> to be employed in the chemical characterization of a solid waste. As has already been emphasized, the appropriate number of samples is the least number of samples required to generate a sufficiently precise estimate of the true mean (μ) concentration of a chemical contaminant of a waste. From the perspective of most waste producers, that means the minimal number of samples needed to demonstrate that the upper limit of the CI for μ is less than the applicable regulatory threshold (RT). The formula for estimating appropriate sampling effort (Table 9-1, Equation 8) indicates that increased sampling effort is generally justified as s^2 or the "$t_{.20}$" value (probable error rate) increases

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and as $\Delta(RT - \bar{X})$ decreases. In a well-designed sampling plan for a solid waste, an effort is made to estimate the values of $\bar{X}$ and s^2 before sampling is initiated. Such preliminary estimates, which may be derived from information pertaining to similar wastes, process engineering data, or limited analytical studies, are used to identify the approximate number of samples that must be collected from the waste. It is always prudent to collect a somewhat greater number of samples than indicated by preliminary estimates of $\bar{X}$ and s^2 since poor preliminary estimates of those statistics can result in an underestimate of the appropriate number of samples to collect. It is usually possible to process and store the extra samples appropriately until analysis of the initially identified samples is completed and it can be determined if analysis of the additional samples is warranted.

9.1.1.3 Basic Sampling Strategies

It is now appropriate to present general procedures for implementing the three previously introduced sampling strategies (simple random sampling, stratified random sampling, and systematic random sampling) and a hypothetical example of each sampling strategy. The hypothetical examples illustrate the statistical calculations that must be performed in most situations likely to be encountered by a waste producer and, also, provide some insight into the efficiency of the three sampling strategies in meeting regulatory objectives.

The following hypothetical conditions are assumed to exist for all three sampling strategies. First, barium, which has an RT of 100 ppm as measured in the EP elutriate test, is the only chemical contaminant of concern. Second, barium is discharged in particulate form to a waste lagoon and accumulates in the lagoon in the form of a sludge, which has built up to approximately the same thickness throughout the lagoon. Third, concentrations of barium are relatively homogeneous along the vertical gradient (from the water-sludge interface to the sludge-lagoon interface), suggesting a highly controlled manufacturing process (little between-batch variation in barium concentrations). Fourth, the physical size of sludge samples collected from the lagoon is as large as practical, and barium concentrations derived from those samples are normally distributed (note that we do not refer to barium levels in the samples of sludge because barium measurements are actually made on the elutriate from EP toxicity tests performed with the samples). Last, a preliminary study of barium levels in the elutriate of four EP toxicity tests conducted with sludge collected from the lagoon several years ago identified values of 86 and 90 ppm for material collected near the outfall (in the upper third) of the lagoon and values of 98 and 104 ppm for material obtained from the far end (the lower two-thirds) of the lagoon.

For all sampling strategies, it is important to remember that barium will be determined to be present in the sludge at a hazardous level if the upper limit of the CI for μ is equal to or greater than the RT of 100 ppm (Table 9-1, Equations 6 and 7).

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9.1.1.3.1 Simple Random Sampling

Simple random sampling (Box 1) is performed by general procedures in which preliminary estimates of $\overline{X}$ and s^2, as well as a knowledge of the RT, for each chemical contaminant of a solid waste that is of concern are employed to estimate the appropriate number of samples (n) to be collected from the waste. That number of samples is subsequently analyzed for each chemical contaminant of concern. The resulting analytical data are then used to conclude definitively that each contaminant is or is not present in the waste at a hazardous concentration or, alternatively, to suggest a reiterative process, involving increased sampling effort, through which the presence or absence of hazard can be definitively determined.

In the hypothetical example for simple random sampling (Box 1), preliminary estimates of $\overline{X}$ and s^2 indicated a sampling effort consisting of six samples. That number of samples was collected and initially analyzed, generating analytical data somewhat different from the preliminary data (s^2 was substantially greater than was preliminarily estimated). Consequently, the upper limit of the CI was unexpectedly greater than the applicable RT, resulting in a tentative conclusion of hazard. However, a reestimation of appropriate sampling effort, based on statistics derived from the six samples, suggested that such a conclusion might be reversed through the collection and analysis of just one more sample. Fortunately, a resampling effort was not required because of the foresight of the waste producer in obtaining three extra samples during the initial sampling effort, which, because of their influence in decreasing the final values of $\overline{X}$, $s_{\overline{X}}$, $t_{.20}$, and, consequently, the upper limit of the CI -- values obtained from all nine samples -- resulted in a definitive conclusion of nonhazard.

9.1.1.3.2 Stratified Random Sampling

Stratified random sampling (Box 2) is conducted by general procedures that are similar to the procedures described for simple random sampling. The only difference is that, in stratified random sampling, values of $\overline{X}$ and s^2 are calculated for each stratum in the population and then integrated into overall estimates of those statistics, the standard deviation (s), $s_{\overline{X}}$, and the appropriate number of samples (n) for all strata.

The hypothetical example for stratified random sampling (Box 2) is based on the same nine sludge samples previously identified in the example of simple random sampling (Box 1) so that the relative efficiencies of the two sampling strategies can be fully compared. The efficiency generated through the process of stratification is first evident in the preliminary estimate of n (Step 2 in Boxes 1 and 2), which is six for simple random sampling and four for stratified random sampling. (The lesser value for stratified sampling is the consequence of a dramatic decrease in s^2, which more than compensated for a modest increase in Δ.) The most relevant indication of sampling efficiency is the value of $s_{\overline{X}}$, which is directly employed to calculate the CI. In the case of simple random sampling, $s_{\overline{X}}$ is calculated as 2.58 (Step 9 in Box 1), and, for stratified random sampling, $s_{\overline{X}}$ is determined to be 2.35 (Steps 5 and 7 in Box 2). Consequently, the gain in efficiency attributable to stratification is approximately 9% (0.23/2.58).

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BOX 1.   STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES
ARE PRESENT AT HAZARDOUS LEVELS - SIMPLE RANDOM SAMPLING

<u>Step</u>   <u>General Procedures</u>

1. Obtain preliminary estimates of $\bar{X}$ and s^2 for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2a and 3a (Table 9-1).

2. Estimate the appropriate number of samples (n_1) to be collected from the waste through use of Equation 8 (Table 9-1) and Table 9-2. Derive individual values of n_1 for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual n_1 values.

3. Randomly collect at least n_1 (or $n_2 - n_1$, $n_3 - n_2$, etc., as will be indicated later in this box) samples from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of $\bar{X}$ and s^2). Maximize the physical size (weight or volume) of all samples that are collected.

4. Analyze the n_1 (or $n_2 - n_1$, $n_3 - n_2$ etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data for obvious departures from normality.

5. Calculate $\bar{X}$, s^2, the standard deviation (s), and $s_{\bar{X}}$ for each set of analytical data by, respectively, Equations 2a, 3a, 4, and 5 (Table 9-1).

6. If $\bar{X}$ for a chemical contaminant is equal to or greater than the applicable RT (Equation 7, Table 9-1) and is believed to be an accurate estimator of μ, the contaminant is considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which $\bar{X}$ is greater than s^2, perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if $\bar{X}$ is about equal to s^2) or the arcsine transformation (if $\bar{X}$ is less than s^2) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 9-1).

7. Determine the CI for each chemical contaminant of concern by Equation 6 (Table 9-1) and Table 9-2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7, Table 9-1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration and the study is completed.   Otherwise, the opposite conclusion is tentatively reached.

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8. If a tentative conclusion of hazard is reached, reestimate the total number of samples (n_2) to be collected from the waste by use of Equation 8 (Table 9-1) and Table 9-2. When deriving n_2, employ the newly calculated (not preliminary) values of x and s^2. If additional $n_2 - n_1$ samples of waste cannot reasonably be collected, the study is completed, and a definitive conclusion of hazard is reached. Otherwise, collect extra $n_2 - n_1$ samples of waste.

9. Repeat the basic operations described in Steps 3 through 8 until the waste is judged to be nonhazardous or, if the opposite conclusion continues to be reached, until increased sampling effort is impractical.

Hypothetical Example

Step

1. The preliminary study of barium levels in the elutriate of four EP toxicity tests, conducted with sludge collected from the lagoon several years ago, generated values of 86 and 90 ppm for sludge obtained from the upper third of the lagoon and values of 98 and 104 ppm for sludge from the lower two-thirds of the lagoon. Those two sets of values are not judged to be indicative of nonrandom chemical heterogeneity (stratification) within the lagoon. Therefore, preliminary estimates of $\bar{X}$ and s^2 are calculated as:

$$\bar{X} = \frac{\sum\limits_{i=1}^{n} X_i}{n} = \frac{86 + 90 + 98 + 104}{4} = 94.50, \text{ and} \qquad \text{(Equation 2a)}$$

$$s^2 = \frac{\sum\limits_{i=1}^{n} X_i^2 - (\sum\limits_{i=1}^{n} X_i)^2/n}{n - 1} \qquad \text{(Equation 3a)}$$

$$= \frac{35,916.00 - 35,721.00}{3} = 65.00.$$

2. Based on the preliminary estimates of $\bar{X}$ and s^2, as well as the knowledge that the RT for barium is 100 ppm,

$$n_1 = \frac{t_{.20}^2 s^2}{\Delta^2} = \frac{(1.638^2)(65.00)}{5.50^2} = 5.77. \qquad \text{(Equation 8)}$$

3. As indicated above, the appropriate number of sludge samples (n_1) to be collected from the lagoon is six. That number of samples (plus three extra samples for protection against poor preliminary estimates of $\bar{X}$ and s^2) is collected from the lagoon by a single randomization process (Figure 9-2). All samples consist of the greatest volume of sludge that

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WASTE OUTFALL

UPPER THIRD
OF LAGOON

LIMIT OF INFLUENCE OF WASTE PLUME

LOWER TWO-THIRDS
OF LAGOON

WASTE LAGOON

OVERFLOW PIPE

IMAGINARY SAMPLING GRID

LEGEND

1—425   Units in Sampling Grid

90   Barium Concentrations (ppm)
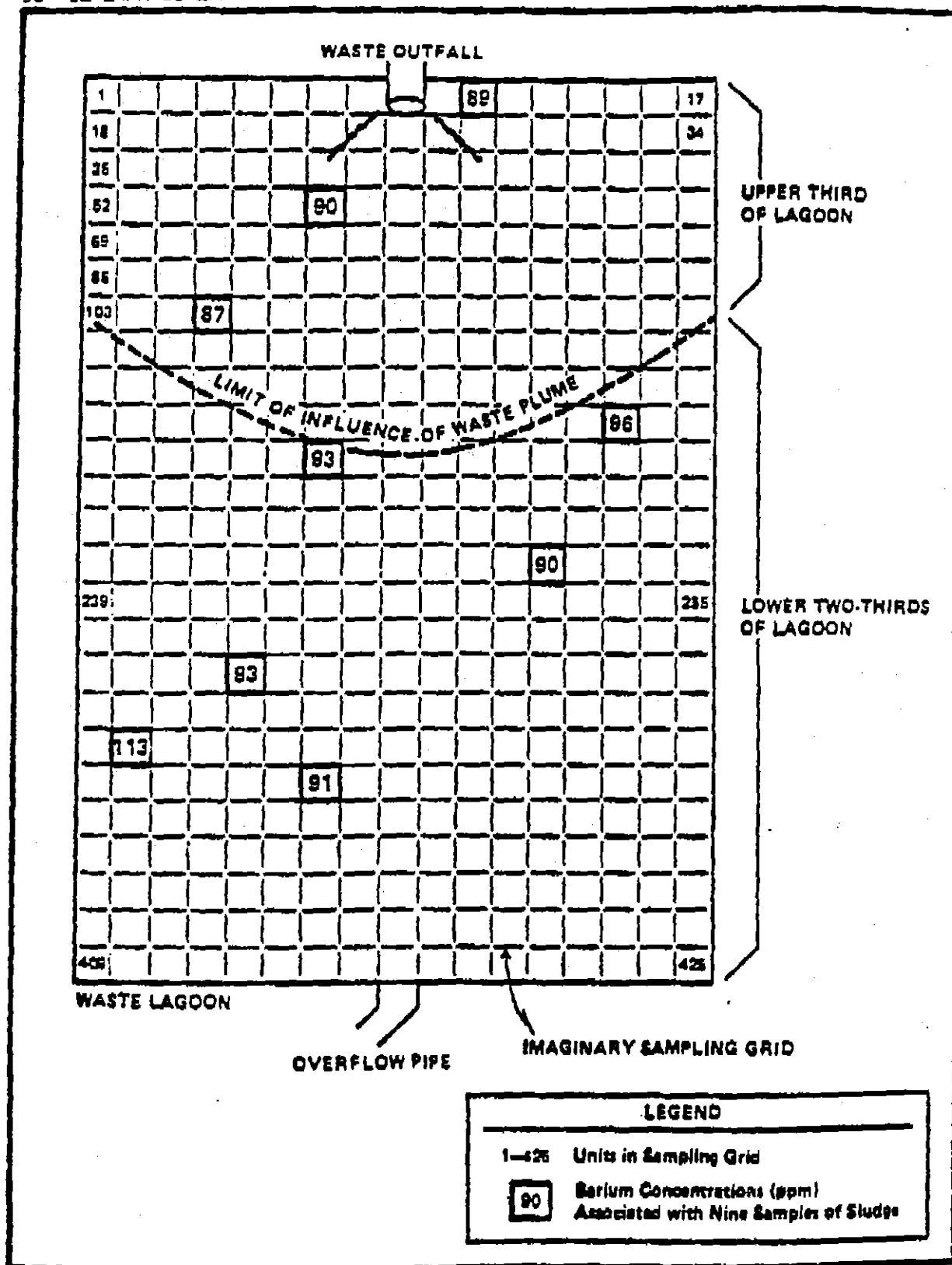Associated with Nine Samples of Sludge

Figure 9-2.—Hypothetical sampling conditions in waste lagoon containing sludge contaminated with barium.
Barium concentrations associated with samples of sludge refer to levels measured in the elutriate of EP toxicity
tests conducted with the samples.

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BOX 2. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES
ARE PRESENT AT HAZARDOUS LEVELS - STRATIFIED RANDOM SAMPLING

Step   **General Procedures**

1. Obtain preliminary estimates of $\overline{X}$ and s^2 for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2b and 3b (Table 9-1).

2. Estimate the appropriate number of samples (n_1) to be collected from the waste through use of Equation 8 (Table 9-1) and Table 9-2. Derive individual values of n_1 for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual n_1 values.

3. Randomly collect at least n_1 (or $n_2 - n_1$, $n_3 - n_2$, etc., as will be indicated later in this box) samples from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of $\overline{X}$ and s^2). If s_k for each stratum (see Equation 3b) is believed to be an accurate estimate, optimally allocate samples among strata (i.e., allocate samples among strata so that the number of samples collected from each stratum is directly proportional to s_k for that stratum). Otherwise, proportionally allocate samples among strata according to size of the strata. Maximize the physical size (weight or volume) of all samples that are collected from the strata.

4. Analyze the n_1 (or $n_2 - n_1$, $n_3 - n_2$ etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data from each stratum for obvious departures from normality.

5. Calculate $\overline{X}$, s_2, the standard deviation (s), and $s_{\overline{x}}$ for each set of analytical data by, respectively, Equations 2b, 3b, 4, and 5 (Table 9-1).

6. If $\overline{X}$ for a chemical contaminant is equal to or greater than the applicable RT (Equation 7, Table 9-1) and is believed to be an accurate estimator of u, the contaminant is considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which $\overline{X}$ is greater than s^2, perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if $\overline{X}$ is about equal to s^2) or the arcsine transformation (if $\overline{X}$ is less than s^2) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 9-1).

7. Determine the CI for each chemical contaminant of concern by Equation 6 (Table 9-1) and Table 9-2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7, Table 9-1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration, and the study is completed. Otherwise, the opposite conclusion is tentatively reached.

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can be practically collected.   The three extra samples are suitably processed and stored for possible later analysis.

4. The six samples of sludge (n_1) designated for immediate analysis generate the following concentrations of barium in the EP toxicity test: 89, 90, 87, 96, 93, and 113 ppm. Although the value of 113 ppm appears unusual as compared with the other data, there is no obvious indication that the data are not normally distributed.

5. New values for $\bar{X}$ and s^2 and associated values for the standard deviation (s) and $s_{\bar{X}}$ are calculated as:

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n} = \frac{89 + 90 + 87 + 96 + 93 + 113}{6} = 94.67, \qquad \text{(Equation 2a)}$$

$$s^2 = \frac{\sum_{i=1}^{n} X_i^2 - (\sum_{i=1}^{n} X_i)^2/n}{n - 1} \qquad \text{(Equation 3a)}$$

$$= \frac{54,224.00 - 53,770.67}{5} = 90.67,$$

$$s = \sqrt{s^2} = 9.52, \text{ and} \qquad \text{(Equation 4)}$$

$$s_{\bar{X}} = s/\sqrt{n} = 9.52/\sqrt{6} = 3.89. \qquad \text{(Equation 5)}$$

6. The new value for $\bar{X}$ (94.67) is less than the RT (100). In addition, $\bar{X}$ is greater (only slightly) than s^2 (90.67), and, as previously indicated, the raw data are not characterized by obvious abnormality. Consequently, the study is continued, with the following calculations performed with nontransformed data.

7. $CI = \bar{X} \pm t_{.20}s_{\bar{X}} = 94.67 \pm (1.476)(3.89) \qquad \text{(Equation 6)}$

    $= 94.67 \pm 5.74.$

Because the upper limit of the CI (100.41) is greater than the applicable RT (100), it is tentatively concluded that barium is present in the sludge at a hazardous concentration.

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8. n is now reestimated as:

$$n_2 = \frac{t_{.20}^2 s^2}{\Delta^2} \quad \frac{(1.476^2)(90.67)}{5.33^2} = 6.95. \qquad \text{(Equation 8)}$$

The value for n_2 (approximately 7) indicates that an additional ($n_2 - n_1 = 1$) sludge sample should be collected from the lagoon.

9.   The additional sampling effort is not necessary because of the three extra samples that were initially collected from the lagoon. All extra samples are analyzed, generating the following levels of barium for the EP toxicity test: 93, 90, and 91 ppm. Consequently, $\bar{X}$, s^2, the standard deviation (s), and $s_{\bar{X}}$ are recalculated as:

$$\bar{X} = \frac{\sum\limits_{i=1}^{n} X_i}{n} = \frac{86 + 90 + \ldots + 91}{9} = 93.56 , \qquad \text{(Equation 2a)}$$

$$s^2 = \frac{\sum\limits_{i=1}^{n} X_i^2 - (\sum\limits_{i=1}^{n} X_i)^2/n}{n - 1} \qquad \text{(Equation 3a)}$$

$$= \frac{79,254.00 - 78,773.78}{8} = 60.03,$$

$$s = \sqrt{s^2} = 7.75, \text{ and} \qquad \text{(Equation 4)}$$

$$s_{\bar{X}} = s/\sqrt{n} = 7.75/\sqrt{9} = 2.58. \qquad \text{(Equation 5)}$$

The value for $\bar{X}$ (93.56) is again less than the RT (100), and there is no indication that the nine data points, considered collectively, are abnormally distributed (in particular, $\bar{X}$ is now substantially greater than s^2). Consequently, CI, calculated with nontransformed data, is determined to be:

$$CI = \bar{X} \pm t_{.20} s_{\bar{X}} = 93.56 \pm (1.397)(2.58) \qquad \text{(Equation 6)}$$

$$= 93.56 \pm 3.60.$$

The upper limit of the CI (97.16) is now less than the RT of 100. Consequently, it is definitively concluded that barium is not present in the sludge at a hazardous level.

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System Requirements

Windows®
386, 486, or Pentium® processor-based personal computer
Microsoft® Windows 3.1, Windows 95, Windows NT(TM) 3.5 or later
8 MB of RAM recommended plus a CD-ROM drive

Macintosh ®
Macintosh 68020-68040: 2 MB of application RAM; Power
Macintosh : 4.5 MB of application RAM plus a CD-ROM drive

UNIX®
Sun™ SPARCstation® workstation

SunOS™ version 4.1.3 or later, Solaris® 2.3 or 2.4

OpenWindows™ (3.0 or later) or the Motif™ window manager

8 MB of disk space for Acrobat Reader

32 MB machine

HP Series 9000 workstation, model 700 or higher

HP-UX 9.0.3 or later

HPVUE desktop environment

6 MB of disk space for Acrobat Reader

32 MB machine
See the README.TXT file on the root directory of the CD for
complete installation instructions.

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